PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶:
A61K 7/42

(11) International Publication Number: WO 98/01107
(43) International Publication Date: 15 January 1998 (15.01.98)

(21) International Application Number:

PCT/BR97/00025

(22) International Filing Date:

4 July 1997 (04.07.97)

(81) Designated States: CA, MX, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

(30) Priority Data:

PI 9602991-9

5 July 1996 (05.07.96)

BR

(71) Applicant (for all designated States except US): INDÚSTRIA E COMÉRCIO DE COSMÉTICOS NATURA LTDA. [BR/BR]; Rodovia Regis Bittencoun, km 293, Itapecerica da Serra, CEP-São Paulo, SP (BR).

(72) Inventors; and

- (75) Inventors/Applicants (for US only): STORK NUNES, Almir [BR/BR]; Apartamento 33, Rua das Perobas, 324, Jabaquara, CEP-São Paulo, SP (BR). CHITARRA SOUZA, Simoni [BR/BR]; Apartamento 331, Rua Estela, 22, Vila Mariana, CEP-São Paulo, SP (BR). MARTINS MATHEUS, Luiz, Gustavo [BR/BR]; Apartamento 8, Rua Visconde de Alcântara, 33, Vila Alpina, CEP-São Paulo, SP (BR).
- (74) Agent: DANNEMANN, SIEMSEN, BIGLER & IPANEMA MOREIRA; Caixa Postal 2142, Rua Marquês de Olinda, 70, CEP-22251-040 Rio de Janeiro, RJ (BR).

Published

With international search report.

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: SKIN MOISTURIZING AND PROTECTIVE COSMETIC COMPOSITIONS

(57) Abstract

The present invention refers to skin moisturizing and protective cosmetic compositions against ultraviolet and infrared radiation, comprising a new active components association, formulated with vehicles and additives already known by themselves. Specifically, these compositions contain an active components set comprising: (a) a physical filter, constituted of coated titanium dioxide and/or titanium dioxide and mica, in a general ratio varying between 0,500 % to 6,000 % by weight; (b) a chemical filter, constituted of at least one component of the group constituted of octyl metoxycinnamate, butyl metoxy dibenzoyl methane, benzophenone 3, in a general ratio varying between 2,700 % to 20,000 % by weight; (c) an antiradicals agent, being this natural melanin, in a general ratio varying between 0,005 % to 1,000 % by weight; (d) a usual moisturizing agent, which can be associated to a usual complementary antiradicals agent, in a general ratio varying between 0,100 % to 2,000 % by weight; (e) oligoelements, which can exhibit moisturizing action, in a general ratio varying between 0,500 % to 5,000 % by weight as active components being the remaining to complete cosmetic composition's 100,000 %, constituted of vehicle and usual additives.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

| AŁ | Albania | ES | Spain | LS | Lesotho | SI | Slovenia |
|----|--------------------------|------|---------------------|------------|-----------------------|-----|--------------------------|
| AM | Апислів | FI | Finland | LT | Lithuania | SK | Slovakia |
| AT | A ustria | FR | France | LU | Luxembourg | SN | Senegal |
| ΑŪ | Australia | GA | Gabon | LV | Latvia | SZ | Swaziland |
| AZ | Azerbaijan | GB | United Kingdom | MC | Monaco | TD | Chad |
| BA | Bosnia and Herzegovina | GE | Georgia | MD | Republic of Moldova | TG | Togo |
| BB | Barbados | GH | Ghana | MG | Madagascar | LT. | Tajikistan |
| BE | Belgium | GN | Guinea | MK | The former Yugoslav | TM | Turkmenistan |
| BF | Burkina Faso | GR | Greece | | Republic of Macedonia | TR | |
| BG | Bulgaria | HU | Hungary | ML | Mali | 11 | Turkey |
| BJ | Benin | IE | Ireland | MN | Mongolia | | Trinidad and Tobago |
| BR | Brazil | IL | brael | MR | Mauritania | UA | Ukraine |
| BY | Belarus | IS | lceland | MW | Malawi | UG | Uganda |
| CA | Canada | IT | Italy | MX | Mexico | US | United States of America |
| CF | Central African Republic | JP | Japan | NE | Niger | UZ | Uzbekistan |
| CG | Congo | KE | Kenya | NL. | Netherlands | VN | Viet Nam |
| СН | Switzerland | KG | Kyrgyzstan | NO | | YU | Yugoslavia |
| CI | Côte d'Ivoire | KP | Democratic People's | NZ. | Norway | ZW | Zimbabwe |
| СМ | Cameroon | 14.5 | Republic of Korea | | New Zealand | | |
| CN | China | KR | Republic of Korea | · PL PT | Poland | | |
| CU | Cuba | KZ | Kazakstan | RO | Portugal | | |
| CZ | Czech Republic | LC | Saint Lucia | RU | Romania | | |
| DE | Germany | ū | Liechtenstein | | Russian Federation | | |
| DK | Denmark | LK | Sri Lanka | SD | Sudan | | |
| EE | Estonia | LR | | SE | Sweden | | |
| -L | Levelle | LK | Liberia | SG | Singapore | | |

WO 98/01107 PCT/BR97/00025

5

10

15

20

SKIN MOISTURIZING AND PROTECTIVE COSMETIC COMPOSITIONS

Technical field

The present invention refers to skin moisturizing and protective cosmetic compositions against ultraviolet and infrared radiation, which contain natural origin melanin pigment as free radicals capturer.

Background art

The photoprotection concept and the skin damages caused by ultraviolet radiation (UV) exposition were already exhaustively studied.

In a simplified form, it is possible to state that UV rays are responsible for collagen fibers destruction and for abnormal elastic fibers production, besides promoting alterations on the dermal microvascularization. Depending on rays intensity and acting depth, the skin suffers degeneration in its structure and abnormalities in its normal pigmentation process. In addition to that, the free radicals formation has an important role in the so called photoaging, due to the attack upon the cutaneous tissue structural molecules as much as due to their self-defense implication, the antioxidant mechanisms.

According to the invention, the new solar protection compositions comprise filters with a much wider protection spectrum, considering also infrared (IR) radiation, whose main biological manifestation is felt in form of heat. Recent studies showed the high damaging potential that this solar spectrum range can cause in synergy with UV radiation.

10

15

20

25

30

35

Besides all already known basic active compounds, the natural origin melanin is also included in the photoprotectives. This compound, skin's normal defense essential substance, is responsible for sunlight absorption and reflection mechanisms, and is capable of promoting free radicals stabilization, which are generated by the incident radiation.

Among the main active components added in the treatment products, it is possible to name the flavonoids contained in a vegetable extract of considerable anti-inflammatory and antiradicals actions. Besides that, skin hydration, exposed to sun, will be recovered through the hydrolipidic mantle reintegration and through the reposition of minerals lost due to excessive drying.

This reports aims to inform the chosen active components main characteristics and functions, considering the main aspects of the claimant's new solar protection compositions.

To complete this presentation the following bibliography was enclosed: "Intensification of Ultraviolet-induced Dermal Damage by Infrared Radiation", Lorraine H.Kligman, published in Arch. Dematol. Res. pages 272:229-238 (1982); "Full Spectrum Solar Radiation as a Cause of Dermal Photodamage UVB to Infrared", Lorraine H.Kligman, published in Acta Derm. Venereol. Stockholm 1987, Suplem 134, pages 53-61; "Cutaneous effects and therapeutic uses of heat with emphasis on infrared radiation", Jeffrey S.Dover, Tania J.Phillips and Kenneth A.Arndt, published in Clinical Review, being the article withdrawn from J.Amer.Acad.of Dermatology, vol.20, nr.2, part 1, (February 1989); "The IR Factor", C.Trullas, C.Pelejero, R.Del Rio and M.Lecha, published in Sun Care (March 1995); "Formulation, Évaluation de Préparations Cosmétiques Réfléchissant Les Infra-Rouges", Aline Fourleignie Ép, Callebert, work published by Université Paris-Sud (Paris XI) - Université René Descartes (Paris) - Université de Lyon I (1984-1985); "Melanin Can Improve Sunscreens", Miles R.Chedekel, published in Cosmetic & Toiletries magazine, Vol.11, nr.1, page 71 (January 1996); "UVA Protection by a Melanin-containing Sunscreen, Measured by the Sunburn Cell Assay", Michael S.Christensen, Peter T.Pugliese, Sue Walmer and Sergio Nacht, published in Melanin: It's Role in Human Photoprotection (1995); and "UVA and UVB Protection against Lipid Peroxidation by a Melanin-containing Sunscreen", Peter T.Pugliese, Michael S.Christensen, Sergio Nacht and Sue Walmer published in Melanin: It's Role in Human Photoprotection (1995). This bibliography is the base of the main informations contained in this report, advocating the main concepts and active components here presented.

15

20

25

30

35

5 Summary of the invention

The Significance Of Protection Against Infrared Rays

Besides UV radiation (100 to 400 nm), the solar spectrum reaching earth's surface is formed by visible light (400 to 700 nm), infrared radiation (700 to 3000 nm) and, in last instance, microwaves and radio waves. The radiations exhibiting the longer wave lengths are the ones with deeper cutis penetration, being almost able of crossing it.

In a curious way, the action of IR rays over the skin was scarcely studied, although they represent approximately 40% of all incident radiation and exhibit significant penetration in the cutaneous layers, even more than UV radiation (they cross epidermis and derma, extinguishing in the hypodermis).

The explanation for this disinterest is based in theoretical considerations which suggest that photochemical reaction are not thermodependent. Notwithstanding, several degeneration processes, associated to biochemical reaction, are extremely thermodependent. This makes IR radiation protection as important as UV protection.

The biological response against IR radiation (which promotes a molecules vibration) is specifically given as a temperature increase. For wave lengths longer than 800 nm, occurs also a photochemical reaction similar to UV.

IR rays increase the damages that would be caused only by UV rays: formation of elastic fibers much different from those resulting in actinic elastosis (they are thinner, being similar to feathers), influence over the dermal collagen quantity with a mucopolysaccharides concentration increase (proportional to irradiation period) and damages in the cellular DNA structure and its restoring mechanism (IR exclusive action), what contributes to an oncogenic action.

The acute IR radiation exposition promotes epidermis lipidic bilayer thickness reduction, erythema with blood vessels dilatation, mastocytes granulation (cells of the organism defense system) and free arachidonic acid and prostaglandines concentration increase, these are mediator agents of the radiation induced inflammatory response. The chronic exposition can cause solar elastosis and lead to cutaneous aging due to actinic action. Thus, IR and UV radiations effects are difficult of being separately considered: they exhibit synergetic actuation on photoaging and photocarcinogenesis.

The knowledge of the damaging effects caused by this non-ionizing radiation obliges technological development in direction to the manufacturing of products also considering this IR radiation.

The active component selected to exert IR protective function is a mineral pigment, capable of reflecting this radiation. Basically, it is a titanium dioxide micronized

15

20

25

30

35

particle, coated with mica (10 to 60 μm diameter), commercially known as Timiron Super Red® (Merck).

Scientific studies showed meaningful results in relation to this pigment activity. The product was compared to several other physical filters (zinc oxide and titanium dioxide with other coatings), exhibiting the best performance in terms of its IR radiation reflection capacity, as also in cutaneous erythema reduction, caused due to solar exposition. According to obtained informations, the reflective agent is capable of producing a 5 to 7°C temperature reduction on the cutaneous surface.

Melanins: natural photoprotectives

When the skin is submitted to sunlight irradiation, several reactions are unleashed, resulting in melanin formation, a non-specific organism response to an external aggression. These reactions occur inside the melanosome, produced by the melanocyte.

The melanins (in fact, a set of different molecules) are organic polymers exhibiting several conjugated double bindings, so that they perform light absorption in the UV, visible light and IR ranges.

Specifically, these wide spectrum pigments perform an uniform UVA radiation absorption, exerting an important role in the direct photoprotection related to this spectrum range.

The melanin added to the photoprotectives contained in the new solar composition, is a natural product obtained through the refinement of cephalopods tincture: Sepia Melanilna® (Melco). It is a non-toxic and hypoallergenic product. It is a photoprotector agent and free radicals capturer, produced by sunlight.

Its main actions are:

- Antioxidant: protects the cells against oxygen metabolites, inhibiting the lipidic peroxidation and exerting an important protective role against oxidative protean damage. In a 0,25% concentration, is capable of inhibiting 71% of the substrate oxidation process. For a brief comparison, 0,10% of vitamin E acetate (considered one of the best antioxidizing agents) reduces the oxidation process in 89%.
- Free radicals capturer: melanin is considered a stable free radical; consequently exhibits an electrons exchange ability. This property enables it to "neutralize" free radicals which can cause cell damage.
- Photoprotection: actuates against erythema, actinic aging and skin cancer.
 Acts together with other filters, helping in the SPF value increase.

Studies showed that photoprotectives containing UVB filters + melanin are excellent protectives against UVA and UVB radiation and lipidic peroxidation, promoting a

15

20

25

30

35

5 15% reduction in the damages caused by UVA rays and a 96,58% reduction in the damages caused by UVB rays.

The incorporation of melanin solid particles, microdispersed in photoprotectives, makes it possible to obtain a 4 units increase in the SPF factor, while increasing the UVA protection (confirmed in clinical tests).

The bioflavonoids (rutin, quercitol, rhamnetol, esculin) are protection factors derived from vitamin P, which are concerned in the capillary permeability process. They exhibit properties against skin aging, inhibiting the action of enzymes responsible for conjunctive tissue degradation (collagenase, elastosis, hyaluronidase). They stimulate the cells mitotic potential and exhibit antiradicals, scaring, repairing and re-balancing properties for the skin damaged by the sun.

Hydration: replacing what the skin needs

The solar exposition promotes a skin tissue temperature increase, resulting in perspiration, leading to water and mineral loss.

Minerals are cofactors of several enzymes which catalyze the cellular reactions (are enzymes functional parts) and assure a normal cellular metabolism. Without them, the enzymes would not function.

As hydrophilic agents for the reposition of the lost hydration, minerals contained in seaweeds extract were chosen: selenium, zinc, chrome, calcium, magnesium, silicon, fluorine, nickel and cobalt.

These elements, also known as oligoelements, participate in the cells normal growth, in the synthesis of proteins precursors and codifiers (RNA and DNA), in the synthesis (zinc and silicon) and transformation (copper) of tropocollagen in collagen, in the transformation of keratin precursor in keratin in the corneal layer and in the electrons transportation in the respiratory chain.

The seaweeds extract active components supply water and electrolytes to the conjunctive tissue, conferring skin turgidity and firmness, increasing skin tension and improving its elasticity. They also react with the corneal layer amino groups, forming protective pellicles and reducing the transepidermal water loss.

These active components, associated to the product basis, are capable of restoring the hydrolipidic mantle damaged by the sun. They belong to the treatment aspect, offered by the present solar protection products invented.

The present invention refers, in particular, to anti-solar emulsions, for skin protection against aggressions caused by UVB, UVA and IR radiation. They have

moisturizing function and their differential is based on the antiradicals action. The main active component is melanin, of natural origin. They are water-resistant products.

Detailed description of the invention

Manufacturing Process

10

15

25

30

35

These compositions are manufactured through usual processing techniques, exception made to the powders dispersion, which requires special attention to avoid posterior agglomeration.

The oily phase or, better, the non-aqueous phase, shall be previously heated at 80°C and, together with titanium dioxide, be submitted to a high efficiency homogenizer, in order to guarantee total pigment dispersion. The coated particle shall not be submitted to trituration.

Also at 80°C, the already dispersed oily phase should be added to the aqueous phase, so that it is possible to proceed to emulsification.

The product should be cooled down at 45°C for the IR filter and melanin incorporation, in order to guarantee these active components action.

The process termination is done through the addition of the remaining formulation ingredients.

Presentation Form

The invention provides fluid emulsions, lightly pigmented (brownish), not oily, not fatty and of easy spreading, in order to guarantee the uniformity of the protective film applied onto the skin.

Action Mechanism

This photoprotectives line contains chemical filters, that protect the skin against the damages caused by UVB and UVA radiation (absorption). The physical filters, with a wider spectrum, are UVB, UVA and IR radiation reflectors.

The natural melanin, in synergy with vitamin E, confers the product free radicals capturing action, neutralizing unstable molecules and avoiding the formation of new ones (chain reaction).

The moisturizing action occurs through oligoelements reposition (micronutrients), which are lost together with the transepidermal water loss (TEWL) when the skin is exposed to the sun (excessive drying).

Formula Basis: Components and Concentrations

Basis Composition

10

15

25

30

35

The here described solar compositions contain, besides their active components, additional materials or additives. These are added to guarantee formulation physicochemical and microbiological stability, as also a pleasant sensorial when the product is applied to the skin.

The additional materials constituting the formulation vehicle, include sequestering, antioxidant and preservative agents, emollients, thickeners/ neutralizers and emulgators, already known by themselves, that can be solid or liquid. Examples of each of these components, that can be used associated or separately, and their usage concentration, include:

• Vehicle: 45,00 to 75,00%

Antioxidant: 0,01 to 0,10%

Preservative: 0,01 to 1,00%

Emollient: 1,00 to 20,00%

Emulgator: 0,10 to 5,00%

Thickener: 0,05 to 1,00%

• Neutralizer: 0,10 to 2,00%

Sequestering agent: 0,05 to 0,50%

As antioxidant, we can name butyl hydroxytoluene (BHT), butyl hydroxyanisole (BHA), di-alpha tocopherol, ascorbic acid, among others.

As preservatives, we can name the parabens, thiazolidines, imidazolidinyl urea, diazolidinyl urea, formaldehyde, benzoic acid, quaternium 15, phenoxyethanol, 2-bromo-2-nitropropane-1,3-diol.

As emollients, we can name isopropyl isostearate, isobutyl palmitate, isocetyl stearate, octyl palmitate, isopropyl laurate, cetyl lactate, isopropyl linoleate, palmitic acid, oleic alcohol, octadecanol, behenyl alcohol, cetyl palmitate, octyl isostearate, isopropyl stearate, alkyl benzoate, mineral oil, lanolin alcohols and derivatives, waxes and vegetable oils, and silicone and their derivatives.

As emulgators, we can name sorbitan, glycerol, waxes and phosphated fatty amines derivatives, acrylic polymers, polyoxiethylenes, polyethylene glycols derivatives, with or without neutralization.

As thickeners, we can name carboxyvinyl polymers, gums, starches, modified aluminium and magnesium silicates, alkylaryl ammonium, esmectitas, cellulose derivatives, hydrated aluminium silicates.

As sequestering agents, we can name ethylenediamine tetraacetic acid (EDTA), ethydronic acid, deferrioxamine, lactoferrine.

5 Active Components

The active components added in the above described photoprotective compositions, are discriminated in several types according to the SPF value (solar protection factor). The following examples are also useful to exemplify the invention:

SPF 4:

10

- chemical filter: octyl metoxycinnamate2,000-4,000%
- chemical filter: butyl metoxy dibenzoyl methane0,200-1,000%
- chemical filter: benzophenone 30,500-1,000%
- physical filter: coated titanium dioxide 0,000-1,000%
- physical filter IV: titanium dioxide and mica 0,500-1,000%

15

- antiradicals agent: natural melanin0,005-1,000%
- antiradicals/moisturizing agent:0,100-2,000%
- moisturizing agent: oligoelements0,500-5,000%

SPF 8:

chemical filter: octyl metoxycinnamate3,000-6,000%

20

- chemical filter: butyl metoxy dibenzoyl methane1,000-2,000%
- chemical filter: benzophenone 31,000-3,000%
- physical filter: coated titanium dioxide 1,000-2,000%
- physical filter IV: titanium dioxide and mica 0,500-1,000%
- antiradicals agent: natural melanin0,005-1,000%

25

- antiradicals/moisturizing agent:0,100-2,000%
- moisturizing agent: oligoelements0,500-5,000%

SPF 15:

- chemical filter: octyl metoxycinnamate5,000-8,000%
- chemical filter: butyl metoxy dibenzoyl methane1,500-3,000%

30

- chemical filter: benzophenone 32,500-4,000%
- physical filter: coated titanium dioxide 1,000-3,000%
- physical filter IV: titanium dioxide and mica 1,000-2,000%
- antiradicals agent: natural melanin0,005-1,000%
- antiradicals/moisturizing agent:0,100-2,000%

35

moisturizing agent: oligoelements0,500-5,000%

SPF 30:

- chemical filter: octyl metoxycinnamate7,000-10,000%
- chemical filter: butyl metoxy dibenzoyl methane2,000-5,000%
- chemical filter: benzophenone 33,000-5,000%

25

30

35

- physical filter: coated titanium dioxide 1,000-4,000%
- physical filter IV: titanium dioxide and mica 1,000-2,000%
- antiradicals agent: natural melanin0,005-1,000%
- antiradicals/moisturizing agents:0,100-2,000%
- moisturizing agent: oligoelements0,500-5,000%

Summing up the referred active components, we obtain the following minimal and maximal values for the four above mentioned types, being:

3,805 to 16,000% for SPF 4

7,105 to 22,000% for SPF 8

11,605 to 28,000% for SPF 15

15 14,605 to 34,000% for SPF 30

(values expressed by weight).

It is possible to verify that the main distinguishing aspect between the associated active components is quantitative, being the concentration crescent from SPF 4 to SPF 30 types.

These values indicate the complementation of the referred active components associations, through the addition of the corresponding quantities necessary to complete 100%, by weight, of formulation additives, usual by themselves, and already above indicated, namely:

The SPF 4 type will be completed with these usual additives, whose conjoint ratio will vary between 96,195% to 84,000%, by weight, in order to complete global composition's 100%.

In an analogous way, the SPF 8 type will be completed with 92,895% to 78,000%, by weight, of these additives.

To complete the SPF 15 type composition, 88,395% to 72,000%, by weight, of the referred formulation additives will be added. For the SPF 30 type composition, 85,395% to 66,000%, by weight, will be added.

The additive sort selection and its percentage in the composition is a routine matter for the cosmetology expert. The addition limits for each additive were already mentioned above.

As already explained, during composition's manufacturing, the first step is the preparation of two phases: an oily phase, in other words, not exactly aqueous, and an aqueous phase. The oily phase, non-aqueous, is prepared first, with the addition of surfactant agent, if suitable, and titanium dioxide pigment (without coating), including heating and mechanical homogenization. The aqueous phase, also heated at 80°C, and

containing the completing ingredients, specially the emulsifying agent, is added to this first prepared oily phase. After final homogenization at a lower temperature (25-45°C), results a light oil-in-water type emulsion, which does not exhibit greasy characteristics, maintaining composition's uniformity in the protective pellicle spread onto the skin.

Conducted Tests

15

20

The solar protection compositions were submitted to usual dermatological tests, which include primary and accumulated dermal irritability, sensitization, phototoxicity and photoallergy. These tests, when exhibiting favorable results as in this present case, guarantee the products innocuousness and confer them the condition of "dermatologist tested".

The products were also submitted to the comedogenicity test, what confers the products the status of "not comedogenic".

To guarantee the products performance/efficiency, "in vivo" tests were performed for the SPF value (declared number) and water resistance determination. The tests results guarantee that the products being discussed find themselves within the predetermined SPF range almost after 80 minutes immersion (methodologies according to USA's FDA).

15

20

25

30

35

5 CLAIMS

- 1. Cosmetic compositions for skin moisturizing and protection against ultraviolet and infrared radiation, <u>characterized</u> by the fact of containing, as active components association, 3,805% to 34,000%, by weight, of the set comprising:
 - (a) a physical filter, constituted of coated titanium dioxide and/or titanium dioxide and mica, in a general ratio varying between 0,500% to 6,000%, by weight;
 - (b) a chemical filter, constituted of at least one component of the group constituted of octyl metoxycinnamate, butyl metoxy dibenzoyl methane, benzophenone 3, in a general ratio varying between 2,700% to 20,000%, by weight;
 - (c) an antiradicals agent, being this natural melanin, in a general ratio varying between 0,005% to 1,000%, by weight;
 - (d) an usual moisturizing agent, which can be associated to an usual complementary antiradicals agent, in a general ratio varying between 0,100% to 2,000%, by weight;
 - (e) oligoelements, which can exhibit moisturizing action, in a general ratio varying between 0,500% to 5,000%, by weight;

as active components, being the remaining to complete cosmetic composition's 100,000%, constituted of vehicle and usual additives.

- 2. Cosmetic composition, according to claim 1, <u>characterized</u> by the fact of containing:
 - (a) 0,000% to 1,000% of coated titanium dioxide and 0,500% to 1,000%, by weight, of titanium dioxide and mica;
 - (b) 2,000% to 4,000%, by weight, of octyl metoxycinnamate, 0,200% to 1,000%, by weight, of butyl metoxy dibenzoyl methane and 0,500% to 1,000%, by weight, of benzophenone 3;
 - (c) 0,005% to 1,000%, by weight, of melanin;
 - (d) 0,100% to 2,000% of moisturizing/antiradicals agent;
 - (e) 0,500%, by weight, of oligoelements, as active components (with SPF 4).
- 3. Cosmetic composition, according to claim 1, characterized by the fact of containing:

- 5
- (a) 1.000% to 2.000%, by weight, of coated titanium dioxide and 0,500% to 1,000%, by weight, of titanium dioxide and mica;
- (b) 3,000% to 6,000%, by weight, of octyl metoxycinnamate, 1,000% to 2,000% of butyl metoxy dibenzoyl methane and 1,000% to 3,000%, by weight, of benzophenone 3;

- (c) 0,005% to 1,000%, by weight, of coated titanium dioxide and 0,500% to 1,000%, by weight, of titanium dioxide and mica;
- (d) 3,000% to 6,000%, by weight, of octyl metoxycinnamate, 1,000% to 2,000% of butyl metoxy dibenzoyl methane and 1,000% to 3,000%, by weight, of benzophenone 3;

15

- (e) 0,005% to 1,000%, by weight, of natural melanin;
- (f) 0,100% to 2,000% of moisturizing/antiradicals agent;
- (g) 0,500% to 5,000%, by weight, of oligoelements, as active components (with SPF 8).
- 4. Cosmetic composition, according to claim 1, characterized by the fact of containing:
 - (a) 1,000% to 3,000%, by weight, and 1,000% to 2,000%, by weight, of titanium dioxide and mica;
 - (b) 5,000% to 8,000%, by weight, of octyl metoxycinnamate, 1,500% to 3,000%, by weight, of butyl metoxy dibenzoyl methane and 2,500% to 4,000%, by weight, of benzophenone 3;

25

- (c) 0,005% to 1,000%, by weight, of natural melanin;
- (d) 0,100% to 2,000%, by weight, of moisturizing/antiradicals agent;
- (e) 0,500% to 5,000%, by weight, of oligoelements, as active components (with SPF 15).

30

- 5. Cosmetic composition, according to claim 1, characterized by the fact of containing:
 - (a) 1,000% to 4,000%, by weight, of coated titanium dioxide and 1,000% to 2,000%, by weight, of titanium dioxide and mica;

35

40

- (b) 7,000% to 10,000%, by weight, of octyl metoxycinnamate, 2,000% to 5,000%, by weight, of butyl metoxy dibenzoyl methane and 3,000% to 5,000%, by weight, of benzophenone 3;
- (c) 0,500% to 1,000%, by weight, of natural melanin;
- (d) 0,100% to 2,000%, by weight, of moisturizing/antiradicals agent;
- (e) 0,500% to 5,000%, by weight, of oligoelements, as active components (with SPF 30).

PCT/BR97/00025

- 6. Cosmetic composition according to claim 1, <u>characterized</u> by the fact that the moisturizing/antiradicals components were chosen between bioflavonoids, specially rutin, quercitol, rhamnetol, esculin.
 - 7. Cosmetic composition according to claim 1, <u>characterized</u> by the fact that the moisturizing action oligoelements are provided by seaweeds extracts and/or by selenium, zinc, chrome, calcium, magnesium, silicon, fluoride, nickel and cobalt mineral compounds.
 - 8. Cosmetic composition according to any of claims 1 to 7, <u>characterized</u> by the fact of compromising the remaining to complete 100,000%, by weight, constituted of 45,000% to 75,000%, by weight, of usual vehicle and at least one complementary additive chosen between:

15

20

10

5

- i. usual antioxidants, in a 0,01 to 0,10% ratio, by weight;
- ii. usual preservatives, in a 0,01 to 1,00% ratio, by weight;
- iii. usual emollients, in a 1,00% to 20,00% ratio, by weight;
- iv. usual emulgators, in a 0,10 to 5,00% ratio, by weight;
- v. usual thickeners, in a 0,05% to 1,00% ratio, by weight;

vi. usual neutralizers, in a 0,10 to 2,00% ratio, by weight;

vii. usual sequestering agents, in a 0,05% to 0,50% ratio, by weight;

- 9. Cosmetic composition according to claim 8, <u>characterized</u> by the fact of including, as vehicle, an aqueous phase, emulsified, oil-in-water type, homogenized.
- 10. Cosmetic composition according to claim 8, <u>characterized</u> by the fact of containing:
 - (i) as antioxidants, at least one component chosen between butyl hydroxytoluene (BHT), butyl hydroxyanisole (BHA), di-alpha tocopherol, ascorbic acid;

(ii) as preservative, at least one component chosen between parabens, thiazolidines, imidazolidinyl urea, diazolidinyl urea, formaldehyde, benzoic acid, quaternium 15, phenoxyethanol, 2-bromo-2-nitropropane-1,3-diol.

- (iii) as emollient, at least one component chosen between alkyl esters C₃-C₁₈ of lactic, lauric, oleic, palmitic, stearic and linoleic acids, palmitic acid, oleic alcohol, octadecanol, behenyl alcohol, alkyl benzoate, mineral oil, lanolin alcohols and derivatives, waxes and vegetable oils, and silicones and their derivatives;
- (iv) as emulgators, at least one component chosen between sorbitan, glycerol, waxes and phosphated fatty amines derivatives, acrylic polymers, polyoxiethylenes derivatives or adducts, polyethylene glycols derivatives, with or without neutralization;

30

35

- (v) as thickeners, at least one component chosen between carboxyvinyl polymers, gums, starches, modified aluminium and magnesium silicates, alkylaryl ammonium compounds, esmectitas, cellulose derivatives, hydrated aluminium silicates;
- (vi) as neutralizers, usual compounds to adjust pH value between 6,5 to 7,5;

10

(vii) as sequestering agents, at least one component chosen between ethylenediamine tetraacetic acid (EDTA), ethydronic acid, deferrioxamine, lactoferrine.

INTERNATIONAL SEARCH REPORT

PCT/BR 97/00025

| A. CLASSI IPC 6 | FICATION OF SUBJECT MATTER A61K7/42 | | |
|--|--|--|---|
| According to | o International Patent Classification(IPC) or to both national classifica | tion and IFC | |
| B. FIELDS | SEARCHED | | |
| Minimum do IPC 6 | cumentation searched (classification system followed by classification A61K | n symbols) | |
| Documentat | tion searched other than minimum documentation to the extent that su | ich documents are included in the fields sea | irched |
| Electronic d | ata base consulted during the international search (name of data bas | se and, where practical, search terms used) | |
| C. DOCUMI | ENTS CONSIDERED TO BE RELEVANT | | |
| Category ° | Citation of document, with indication, where appropriate, of the rele | vant passages | Relevant to claim No. |
| Α | GB 2 206 282 A (NEUTROGENA CORPOR January 1989 see the whole document | ATION) 5 | 1-10 |
| A,P | US 5 571 503 A (MAUSNER) 5 Novemb see column 4, line 35 - line 39 | per 1996 | 1~10 |
| A | EP 0 518 773 A (L'OREAL) 16 Decem see the whole document | nber 1992 | 1-10 |
| | | | |
| | | | |
| Furt | her documents are listed in the continuation of box C. | X Patent family members are listed | in annex. |
| "A" docume consider a docume which critation of docume other "P" docume of the country of the co | ent which may throw doubts on priority claim(s) or is cited to establish the publication date of another in or other special reason (as specified) sent referring to an oral disclosure, use, exhibition or means ent published prior to the international filing date but | "T" later document published after the inte or priority date and not in conflict with cried to understand the principle or the invention. "X" document of particular relevance; the cannot be considered novel or cannot involve an inventive step when the document of particular relevance; the cannot be considered to involve an indocument is combined with one or minerts, such combined with one or minerts, such combination being obvious the art. "8" document member of the same patent | the application but early underlying the claimed invention to considered to countries taken alone claimed invention wentive step when the ore other such docu—us to a person skilled. |
| | han the priority date claimed actual completion of the international search | Date of mailing of the international see | |
| 2 | 21 November 1997 | 18/12/1997 | |
| Name and | matting address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Eav. (+31-70) 340-3016 | Fischer, J.P. | |

INTERNATIONAL SEARCH REPORT

| information on | patent family | / members |
|----------------|---------------|-----------|
|----------------|---------------|-----------|

PCT/BR 97/00025

| | | 101/BK 9//00025 | | |
|--|------------------|---|--|--|
| Patent document cited in search report | Publication date | Patent tamily member(s) | Publication date | |
| GB 2206282 A | 05-01-89 | US 4820508 A CA 1339009 A | 11-04-89 25-03-97 | |
| US 5571503 A | 05-11-96 | NONE | | |
| EP 518773 A | 16-12-92 | FR 2677544 A AT 118164 T CA 2071276 A DE 69201359 D DE 69201359 T ES 2068012 T JP 5186323 A | 18-12-92 15-02-95 15-12-92 23-03-95 24-05-95 01-04-95 27-07-93 | |